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BOX PATENT APPLICATION
Washington, D.C. 20231

Sir:

Transmitted herewith for filing under 37 CFR 1.53(b) is the

- ☐ patent application of
☐ continuation patent application of
☒ divisional patent application of
☐ continuation-in-part patent application of

Inventors: JIN-KUO HO; CHARNG-SHYANG JONG; CHAO-NIEN HUANG; CHIN-YUAN CHEN; CHIENCHIA CHIU;
CHENN-SHIUNG CHENG; KWANG KUO SHIH

For: OHMIC CONTACT TO SEMICONDUCTOR DEVICES AND METHOD OF MANUFACTURING THE SAME

- ☒ This application claims priority from each of the following Application Nos./filing dates:

USSN 09/325,240, filed June 3, 1999

the disclosure(s) of which is (are) incorporated by reference.

- ☒ Please amend this application by adding the following before the first sentence: "This application is a ☒ division ☐ continuation-in-part of and claims the benefit of U.S. Application No. 09/325,240, filed June 3, 1999, the disclosure of which is incorporated by reference."

Enclosed are:

- ☒ 10 page(s) of specification
☒ 4 page(s) of claims
☒ 1 page of Abstract
☒ 3 sheet(s) of ☒ formal ☐ informal drawing(s).

An assignment (from parent application) of the invention to Industrial Technology Research Institute

- ☒ A ☒ signed ☐ unsigned Declaration & Power of Attorney (from parent application)

- ☐ A ☐ signed ☐ unsigned Declaration.

A verified statement to establish small entity status under 37 CFR 1.9 and 37 CFR 1.27 ☐ is enclosed ☐ was filed in the prior application and small entity status is still proper and desired.

A certified copy of a _____ application.

Information Disclosure Statement under 37 CFR 1.97.

A petition to extend time to respond in the parent application.

Notification of change of ☐ power of attorney ☐ correspondence address filed in prior application.

- ☒ Please cancel claims 1-7

	(Col. 1)	(Col. 2)	
FOR:	NO. FILED	NO. EXTRA	
BASIC FEE			
TOTAL CLAIMS	20 - 20	= *0	
INDEP. CLAIMS	2 - 3	= *0	
<input type="checkbox"/> MULTIPLE DEPENDENT CLAIM PRESENTED			

* If the difference in Col. 1 is less than 0, enter "0" in Col. 2.

Attorney Docket No. 82666-000100US

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Respectfully submitted,
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OHMIC CONTACT TO SEMICONDUCTOR DEVICES AND
METHOD OF MANUFACTURING THE SAME

BACKGROUND OF THE INVENTION

5 Field of the invention

This invention relates to an ohmic contact to semiconductor devices and its manufacturing method, particularly an ohmic contact to p-type gallium nitride and the method of manufacturing the same.

10 Description of prior art

In recent years, gallium nitride (hereinafter referred to as GaN) has been broadly used in the fabrication of short-wavelength light-emitting diodes, laser diodes, photo-detectors and microelectronic components, etc. Good ohmic contact is especially important to commercialized light-emitting devices. Currently, the specific contact resistance for n-type GaN has been reduced to about $10^{-4} \sim 10^{-8} \Omega \cdot \text{cm}^2$. As for p-type GaN, however, the specific contact resistance can only attain $10^{-2} \sim 10^{-3} \Omega \cdot \text{cm}^2$, much higher than that for the contact to n-type GaN. Such a high interface resistance markedly affects the performance and reliability of these devices. Therefore, it is an important issue for the scientists and engineers to lower the specific contact resistance of the contact to p-type GaN. Until now, most conventional methods to manufacture contacts to p-type GaN deposit the metals directly. For example, in US patent no. 5,652,434, the

Nichia Chemical Industrial Company uses Ni or Ni/ Au in its light-emitting diodes (LED) to form a contact. In addition, in US patent no. 5,739,554, Cree Research Company uses Ti/Au, Ti/Ni or Ni/Au in its LED to form contact. But neither described the specific contact resistance of the contacts. In other references, other kinds of metals are disclosed, such as Au, Ni, Ti, Pd, Pt, W, WSi_x, Ni/Au, Pt/Au, Cr/Au, Pd/Au, Au/Mg/Au, Pd/Pt/Au, Ni/Cr/Au, Ni/Pt/Au, Pt/Ni/Au, Ni/Au-Zn, Ni/Mg/Ni/Si, etc. However, the specific contact resistance of the above metal contacts can only attain 10^{-2} ~ 10^{-3} cm⁻², which is higher than 10^{-4} cm⁻² generally required for optoelectronic devices. In addition, almost all of the above metals do not exhibit ohmic behavior.

SUMMARY OF THE INVENTION

Accordingly, the object of this invention is to provide an ohmic contact to semiconductor devices and its manufacturing method by which the interface resistance of ohmic contact is lowered so as to improve the performance and reliability of semiconductor devices.

This invention provides a new semiconductor manufacturing process which can form an ohmic contact to p-type GaN with a low interface resistance for application in the fabrication of GaN-based devices.

The manufacturing method of this invention forms a film, which includes transition metal and noble metal, on the semiconductor substrate. Then, the film is heat-treated and oxidized to obtain an

ohmic contact with a low specific contact resistance. So formed, an ohmic contact can meet the requirement of an optoelectronic device; that is, the specific contact resistance of the ohmic contact is lower than 10^{-2} cm².

5

BRIEF DESCRIPTION OF THE DRAWINGS

The following detailed description, given by way of example and not intended to limit the invention solely to the embodiments described herein, will best be understood in conjunction with the accompanying drawings in which:

Fig. 1 is a diagram illustrating the structure of an ohmic contact according to one embodiment of the invention;

Fig. 2 is a diagram illustrating the structure of an ohmic contact according to another embodiment of the invention;

Fig. 3a is diagram illustrating a pattern formed on a substrate in the CTLM measurement used in this invention;

Fig. 3b illustrates the current-voltage (I-V) measurement of Ni-Au contacts formed on p-type GaN and heat-treated in various ambiances; and

Fig. 4 shows the specific contact resistance obtained by oxidizing Ni/Au layers of different thickness.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The method of fabricating an ohmic contact to semiconductors according to this invention includes the steps of: coating a transition metal and a noble metal or an alloy thereof on a semiconductor material, then heat-treating the metal layer in an oxidizing ambience so that the transition metal is oxidized to form an oxide.

The semiconductor described above is p-type GaN. The transition metal can be Ni, Mn, Cr, Cu, Fe, Co or Pd, etc. The noble metal can be Au, Pt, Rh, Ru, or Ir, etc.

The oxide mentioned above is a single oxide, or a mixture of various oxides such as NiO/CoO or a solid solution of various oxides such as $\text{Ni}_x\text{Co}_{1-x}\text{O}$ ($0 < x < 1$) etc.. The metal in the above film can be a single metal, or various metals or an alloy thereof.

Another layer of metal can be further formed thereon. Such layer of metal can be a single metal such as Au or Ni, a plurality of layers of metals, or a layer of alloy such as Cr/Au or Ti/Pt/Au, etc., for connecting with other circuits.

The ohmic contact formed by the above method has different structures according to different preparation methods of the transition metal and the noble metal. In the first embodiment, after heat-treatment, the transition metal and the noble metal formed on the semiconductor material 10 becomes a mixture of semiconductor oxide 12 and metal 14 as shown in Fig. 1.

In the first embodiment, the above semiconductor material 10 is

formed on a sapphire substrate, with an undoped GaN layer and a GaN layer doped with Mg, each 2 μm thick, formed by MOCVD method. Using this semiconductor material as a test sheet, it is heat-treated in a nitrogen atmosphere to make the Mg doped GaN layer become p-type. This test sheet has an electron concentration of $1 \times 10^{17} \text{ cm}^{-3}$ for its undoped GaN layer and a hole concentration of $2 \times 10^{17} \text{ cm}^{-3}$ for its p-type GaN. A CTLM (circular transmission line model) method is used in the invention to calculate the specific contact resistance (ρ_c).

Next, the fabrication and measurement procedure for the ohmic contact of this invention is described, which includes the steps of: (i) forming a photoresist layer on the GaN with a CTLM pattern; (ii) removing the GaN surface oxide by dipping the test sheet in a solution of $\text{HCl}:\text{H}_2\text{O} = 1:1$ for 3 minutes, then blowing dry the GaN and putting the test sheet immediately into a vacuum chamber of an electron-gun coating system; (iii) degassing the chamber of the electron-gun coating system to a high vacuum, then proceeding with the coating of various metals; (iv) lifting-off a part of metal film to form a metal pattern as shown in Fig. 3(a); (v) heat-treating the test sheet in air, oxygen, 10% H_2 - 90% N_2 or nitrogen atmosphere, in which the temperature is from 200°C to 900°C, and the time is 10 minutes; (vi) conducting I- V measurement for the test sheet; and (vii) analyzing the ρ_c values.

Next, the CTLM measurement and analysis used in the above steps is described, in which the measurement of I-V characteristic to respectively is used to figure out the resistance between the metals

within the inner ring and outside the outer ring of two concentric circles. The analysis of ρ_c is conducted on the I-V curves of ± 0.5 V and ± 20 mV. Generally speaking, the contact structures of this invention exhibits ohmic behavior within the above testing range, i.e., it is provided with a linear I- V curve. Therefore, the specific contact resistance can be calculated through the slope of the curve. The formula of calculating ρ_c for the CTLM method is as follows:

$$R_t = (R_{sh}/2\pi) [\ln(R/r) + L_t(r^{-1} + R^{-1})]$$

$$\rho_c = R_{sh} \times L_t^2$$

where R_t serves as the total resistance of the I- V measurement, R_{sh} is the sheet resistance, and r and R respectively represent the radius of the inner and outer concentric circles, L_t is the transfer length. According to the above formula, a diagram can be formed through R_t of the I- V measurement to the $\ln(R/r)$. Then a linear curve can be obtained by processing the diagram with the least square linear curve fitting method. The slope of the obtained curve is $R_{sh}/2\pi$. The intercept can thus be calculated by the formula when R equals to r , to be $R_{sh}L_t/r\pi$, so that R_{sh} and L_t can be figured out to further calculate ρ_c .

Fig. 3b illustrates the measurement results of this invention, which shows the I- V characteristic of Ni/Au contacts formed on p-type GaN and heat-treated in various atmospheres, wherein curve A represents the situation in which Ni/Au is heat-treated in air or oxygen atmosphere, curve B, in nitrogen atmosphere, and curve C, in 10% H_2 -90% N_2 atmosphere. The temperature of the heat treatment process is 500

°C and the heat-treating time is 10 minutes. The slope of the curve is a maximum, that is, the ρ_s value is a minimum, and the positive current and the negative current is symmetrical to the original point after oxidizing the Ni/Au film. On the other hand, the Ni/Au layer is still a metal film after the test sheet is heat-treated in nitrogen or 10% H_2 -90% N_2 . This results in an increase in the obtained ρ_c . The I-V curve does not maintain linearity when the metal contact is biased at a higher voltage, and the positive and negative currents are not symmetrical to each other. Please also refer to the following Table 1, in which the Ni/Au thin film heat-treated in air of this embodiment still displays a good conductivity.

Table 1

Condition	Sheet resistance (Ω/\square)	Resistivity ($\mu\Omega \cdot \text{cm}$)
As- deposited	11.87	17.8
N_2 , 500°C, 10 min	16.82	25.2
Air, 500°C, 10 min	38.94	97.4

Fig. 4 shows the specific contact resistance of the contacts formed by oxidizing Ni/Au layers of various thicknesses on the p-type GaN, wherein, curve A' represents that Ni is 50 nm and Au is 125 nm, curve B' represents that Ni is 10 nm and Au is 25 nm, curve C' represents that Ni is 10 nm and Au is 5 nm. The oxidation of the above process is heating the test sheet in air for 10 minutes. According to the current experimental data, the minimum specific contact resistance is $1.0 \times 10^{-4} \Omega \cdot \text{cm}^2$.

Using X-ray diffraction to analyze the Ni(10 nm)/Au(5 nm) films heat-treated at 500°C for 10 minutes, the result shows that Ni converts to NiO and Au is still metallic after heat-treated in air. On the contrary, when the test sheet is heat-treated in nitrogen or 10% H₂-90% N₂, the Ni/Au film is still metallic, but the ρ_c value is about 10⁻¹ to 10⁻² $\Omega \cdot \text{cm}^2$. Furthermore, if instead of the above Ni(10 nm)/Au(5 nm), a 50 nm thick Ni film is coated on the p-type GaN and then the same oxidation process is performed to form NiO, and the specific contact resistance of the NiO contact to p-type GaN is measured to analyze the effect of NiO, the ρ_c value is only about 0.1 $\Omega \cdot \text{cm}^2$, but its I-V curve is a linear curve over a wide range. This means that an ohmic contact is formed between NiO and p-GaN. However, the ρ_c value is high since the NiO thus formed is highly resistant. This indicates that the existence of NiO causes the oxidized Ni/Au film form an ohmic contact. Au primarily gives the thin film with an excellent conductivity, because Au can not form an excellent ohmic contact to p-type GaN. According to the prior art, it has been reported that ρ_c is only 53 $\Omega \cdot \text{cm}^2$ (L. L. Smith, et al, J. Mater. Res. 12, 2249(1997)) and $2.6 \times 10^{-2} \Omega \cdot \text{cm}^2$ (T. Mori et al., Appl. Phys. Lett. 69, 3537(1996)) for Au contacts. It has also been reported that stoichiometric NiO is insulating, but becomes p-type if doping with Li⁺ or creating Ni³⁺ ion vacancies in the NiO. Doping NiO with Li₂O can reduce its resistivity to 0.1 $\Omega \cdot \text{cm}$ (Z. M. Jarzebski, Oxide Semiconductors (Pergamon press, Oxford, 1973), Chap. 10). Ni²⁺ ion vacancies formed during the oxidization of Ni create

holes (N. Birks and G. H. Meier, Introduction to High Temperature Oxidation of Metals (Edward Arnold, London, 1983), Chap. 4). Therefore, it is inferred that NiO formed in the oxidized Ni/Au is a p-type semiconductor. Au and P-type NiO, which are in a condition of mixed morphology, have a low interface resistance with P-type GaN and can form an ohmic contact to P-type GaN. Hence, Ni/Au film can form an ohmic contact to p-type GaN after oxidation and heat-treatment, and is provided with a low specific contact resistance.

According to the above inference, any thin film including p-type semiconductor oxide and Au can form an excellent ohmic contact with p-type GaN. In addition to NiO, many oxides can be used to form a p-type semiconductor such as MnO, FeO, Fe₂O₃, CoO (Z. M. Jarzebski, Oxide Semiconductors (Pergamon press, Oxford, 1973), Chap. 11), PdO (R. Uriu et al., J. Phys. Soc. Jpn 60, 2479 (1991)), CuAlO₂ (H. Kawazoe et al., Nature 389, 939 (1997)), SrCu₂O₂ (A. Kudo et al., Appl. Phys. Lett. 73, 220 (1998)), Rh₂O₃ (A. Roy and J. Ghose, Mater. Res. Bull 33, 547 (1998)), CrO, Cr₂O₃, CrO₂, CuO, Cu₂O, SnO, Ag₂O, LaMnO₃, or YBa₂Cu₄O₈, etc.; therefore, it is also possible to form an ohmic contact to p-type GaN using a mixture of this kind of oxide and Au. Furthermore, Au can be replaced by other metals if the metal does not oxidize after heat-treatment. Normally, any noble metal can be used, for example, Au, Pt, Rh, Ru, and Ir, etc.

Referring to Fig. 2, since the interface impedance of the p-type semiconductor oxide and p-type GaN is very low, and the metal can form

an ohmic contact having a low resistivity with the p-type semiconductor oxide, another embodiment of this invention comprises sequentially forming a layer of p-type semiconductor oxide 12 and a layer of metal 24 on the p-type GaN 10 to form an ohmic contact to p-type GaN, such as p-GaN/p-NiO/Cr/Au, etc.

In the above embodiments, the ohmic contact to p-type GaN is described. However, the method of fabricating an ohmic contact can be applied in practice to p-type $\text{Al}_x\text{Ga}_y\text{In}_z\text{N}$ material, where $0 < x, y, z < 1$, and $x + y + z = 1$.

In the past, the specific contact resistance of a contact formed on p-type GaN could attain only $10^{-2} \sim 10^{-3} \Omega \cdot \text{cm}^2$, but the ohmic contact of this invention can obtain a much lower interface resistivity of $1.0 \times 10^{-4} \Omega \cdot \text{cm}^2$. This improvement has been applied to the fabrication of LEDs and GaN based laser diodes with good performance.

Furthermore, the metal formed on the semiconductor material in the last embodiment can be replaced by a transparent conductive film, such as indium-tin oxide (ITO), ZnO or ZnO doped with Ga, In, Al or Ce, etc.

While the present invention has been particularly shown and described with reference to a preferred embodiment, it will be readily appreciated by those of ordinary skill in the art that various changes and modifications may be made without departing from the spirit and scope of the invention. It is intended that the claims be interpreted to cover the disclosed embodiment, those alternatives which have been discussed above and all equivalents thereto.

What is claimed is

- 1 1. A method for manufacturing ohmic contact to a semiconductor
2 including the steps of: forming a plurality of metals on a semiconductor
3 material; heat-treating the plurality of metals in an oxidizing
4 environment so that at least one of the plurality of metals is oxidized
5 to form a p-type semiconductor oxide.
6
- 1 2. A manufacturing method as claimed in claim 1 wherein the
2 semiconductor material is p-type $\text{Al}_x\text{Ga}_y\text{In}_z\text{N}$, and $0 < x, y, z < 1$, and $x + y + z$
3 $= 1$.
4
- 1 3. A manufacturing method as claimed in claim 1 wherein the plurality
2 of metals includes at least a transition metal which can transform into
3 a p-type semiconductor oxide.
4
- 1 4. A manufacturing method as claimed in claim 1 wherein the plurality
2 of metals includes at least a noble metal which is one of Au, Pt, Rh,
3 Ru, and Ir.
4
- 1 5. A manufacturing method as claimed in claim 1 wherein the film formed
2 on the semiconductor material can be an alloy of transition metal and
3 noble metal.
4

1 6. A manufacturing method as claimed in claim 2 wherein the
2 semiconductor material is p-type GaN.

1 7. A manufacturing method as claimed in claim 3 wherein the transition
2 metal is one of Ni, Mn, Fe, Co, Cr, Cu and Pd.

1 8. An ohmic contact to a semiconductor which is formed on a
2 semiconductor material, including a mixture of p-type semiconductor
3 oxide and metal.

1 9. An ohmic contact as claimed in claim 8 wherein the p-type
2 semiconductor oxide includes a single oxide.

1 10. An ohmic contact as claimed in claim 8 wherein the p-type
2 semiconductor oxide includes a mixture of various oxides.

1 11. An ohmic contact as claimed in claim 8 wherein the p-type
2 semiconductor oxide includes a solid solution of various oxides.

1 12. An ohmic contact as claimed in claim 8 wherein the semiconductor
2 material is p-type $\text{Al}_x\text{Ga}_y\text{In}_z\text{N}$, and $0 < x, y, z < 1$, and $x + y + z = 1$.

1 13. An ohmic contact as claimed in claim 8 wherein the p-type
2 semiconductor oxide is one of NiO, MnO, FeO, Fe_2O_3 , CoO, CrO, Cr_2O_3 , CrO_2 ,

CuO, Cu₂O, SnO, Ag₂O, CuAlO₂, SrCu₂O₂ and PdO.

14. An ohmic contact as claimed in claim 8 wherein the metal is Au, Pt, Rh, Ru, or Ir.

15. An ohmic contact as claimed in claim 12 wherein the semiconductor material is p-type GaN.

16. An ohmic contact to a semiconductor, which is formed on a semiconductor material, including a layer of p-type semiconductor oxide and a conductive layer.

17. An ohmic contact as claimed in claim 16 wherein the semiconductor material is p-type Al_xGa_yIn_zN, and 0 < x, y, z < 1, and x + y + z = 1.

18. An ohmic contact as claimed in claim 16 wherein the p-type semiconductor oxide is one of NiO, MnO, FeO, Fe₂O₃, CoO, CrO, Cr₂O₃, CrO₂, CuO, Cu₂O, SnO, Ag₂O, CuAlO₂, SrCu₂O₂, LaMnO₃, YBa₂Cu₄O₈ and PdO.

19. An ohmic contact as claimed in claim 16 wherein the layer of semiconductor oxide includes a single oxide layer.

20. An ohmic contact as claimed in claim 16 wherein the layer of semiconductor oxide includes a plurality of layers of oxides of the

3 same conductivity type.

4

1 21. An ohmic contact as claimed in claim 16 wherein the layer of
2 semiconductor oxide includes a mixture layer of various oxides.

3

1 22. An ohmic contact as claimed in claim 16 wherein the layer of
2 semiconductor oxide includes a solid solution layer consisting of
3 various oxides.

4

1 23. An ohmic contact as claimed in claim 16 wherein the conductive layer
2 includes a single metal layer.

3

1 24. An ohmic contact as claimed in claim 16 wherein the conductive layer
2 includes a plurality of metal layers.

3

1 25. An ohmic contact as claimed in claim 16 wherein the conductive layer
2 is a transparent conductive film.

3

1 26. An ohmic contact as claimed in claim 17 wherein the semiconductor
2 material is p-type GaN.

3

1 27. An ohmic contact as claimed in claim 25 wherein the transparent
2 conductive film is conductive oxide, including indium-tin oxide, ZnO
3 and ZnO doped with Ga, In, Al or Ce.

10

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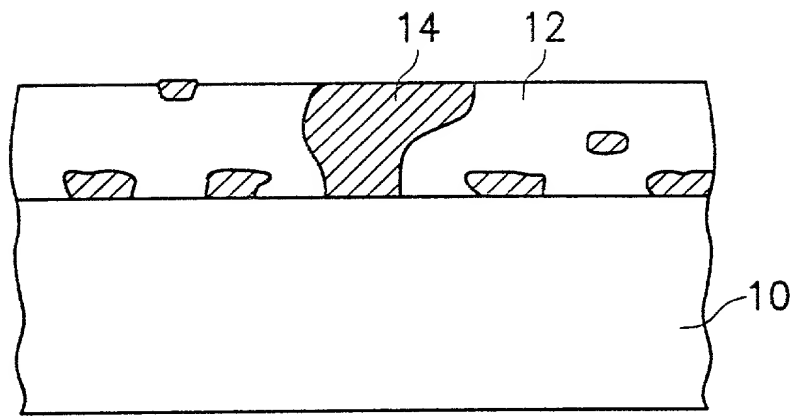


Fig. 1

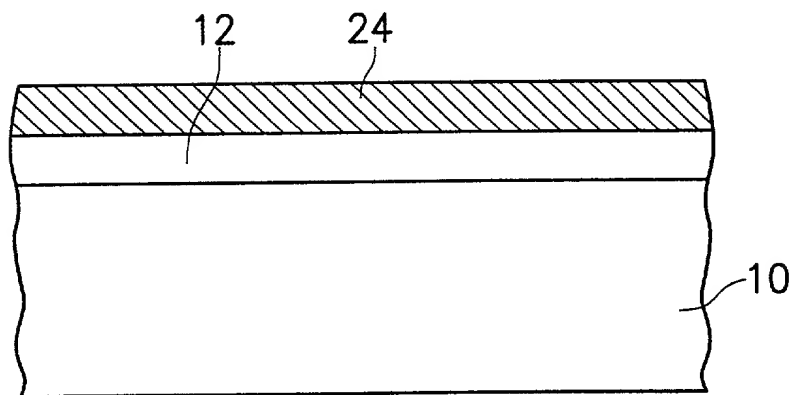


Fig. 2

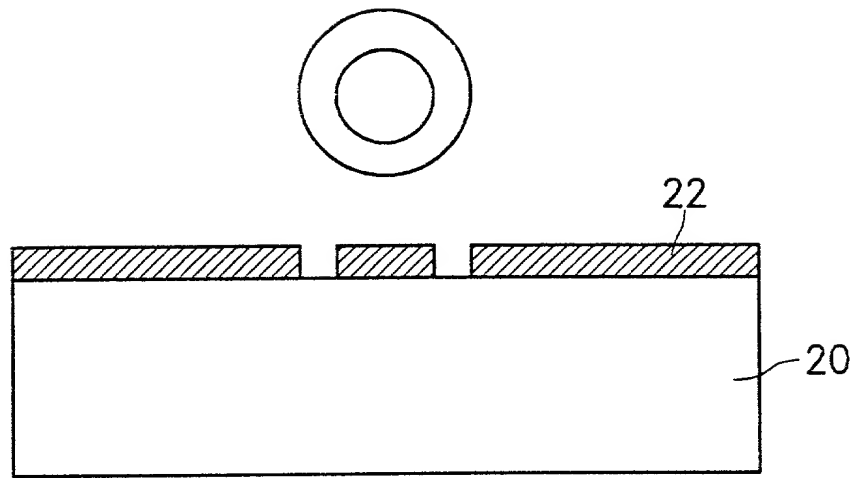


Fig. 3a

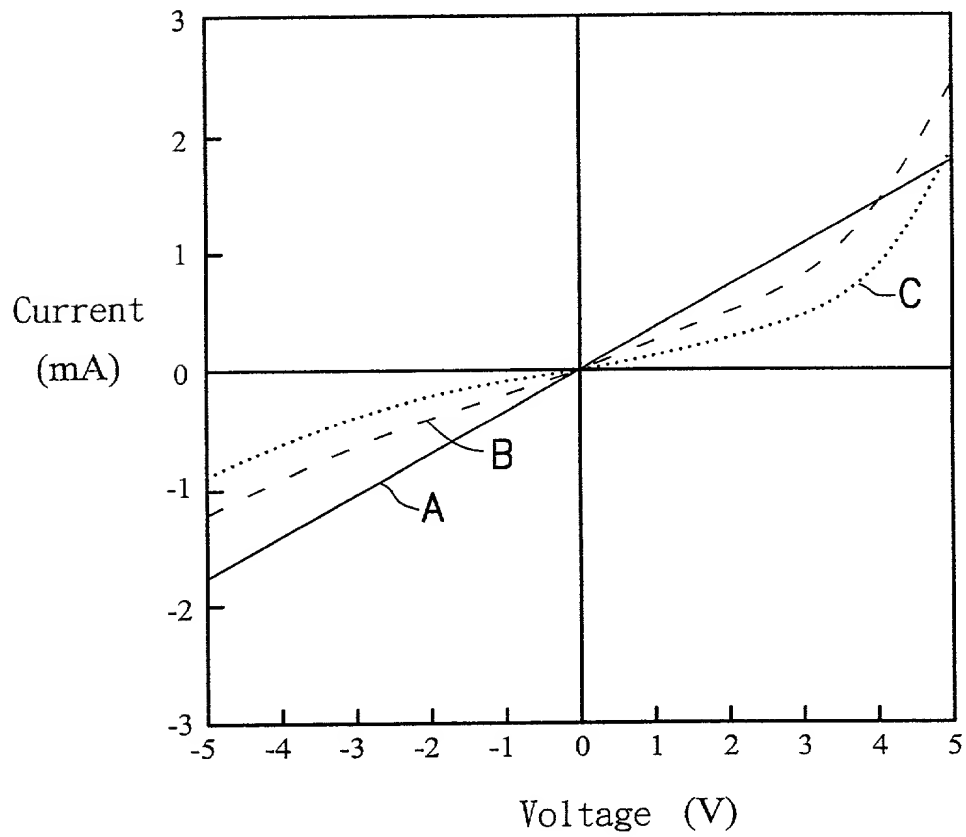


Fig. 3b

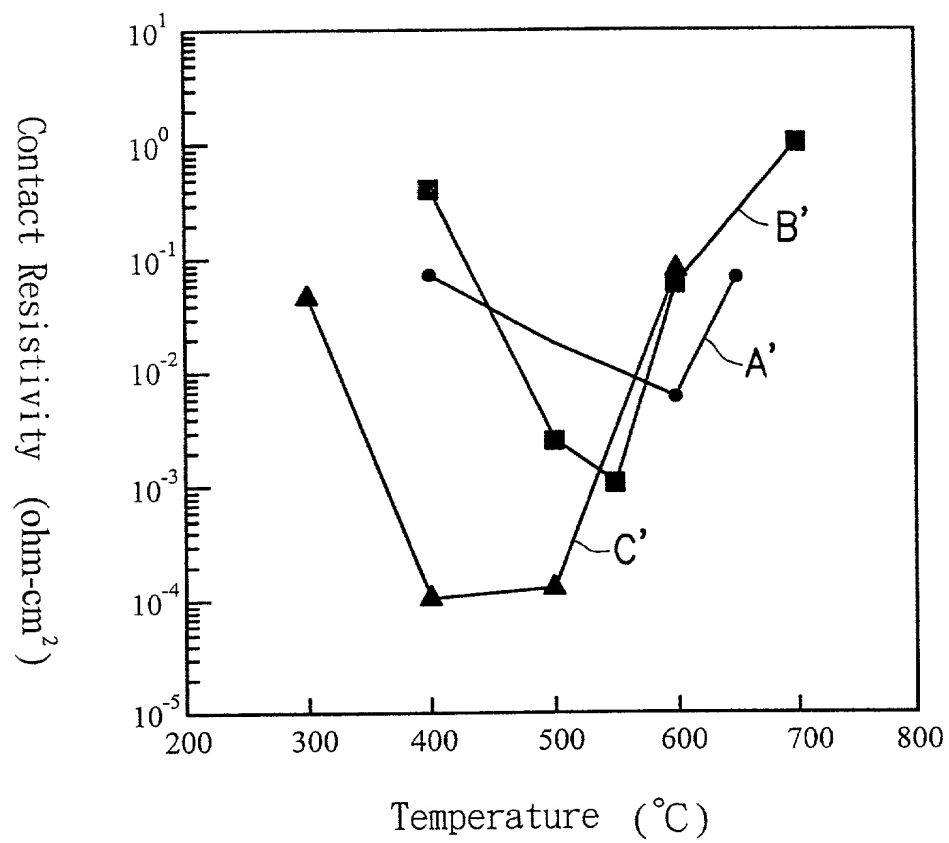


Fig. 4

DECLARATION AND POWER OF ATTORNEY

As a below named inventor, I declare that:

My residence, post office address and citizenship are as stated below next to my name; I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural inventors are named below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

OHMIC CONTACT TO SEMICONDUCTOR DEVICES AND METHOD OF MANUFACTURING THE SAME

the specification of which X is attached hereto or was filed on as Application No. and was amended on (if applicable).

I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above. I acknowledge the duty to disclose information which is material to the examination of this application in accordance with Title 37, Code of Federal Regulations, Section 1.56. I claim foreign priority benefits under Title 35, United States Code, Section 119 of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed.

Prior Foreign Application(s)

Country	Application No.	Date of Filing	Priority Claimed Under 35 USC 119
Taiwan, R.O.C.	87117694	October 26, 1998	Yes <u>X</u> No <u> </u>
			Yes <u> </u> No <u> </u>

I hereby claim the benefit under Title 35, United States Code § 119(e) of any United States provisional application(s) listed below:

Application No.	Filing Date

I claim the benefit under Title 35, United States Code, Section 120 of any United States application(s) listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35, United States Code, Section 112, I acknowledge the duty to disclose material information as defined in Title 37, Code of Federal Regulations, Section 1.56 which occurred between the filing date of the prior application and the national or PCT international filing date of this application:

Application No.	Date of Filing	Status
		<u> </u> Patented <u> </u> Pending <u> </u> Abandoned
		<u> </u> Patented <u> </u> Pending <u> </u> Abandoned

POWER OF ATTORNEY: As a named inventor, I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and transact all business in the Patent and Trademark Office connect therewith.

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I further declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

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Date <i>May 10, 1999</i>	Date <i>May 10, 1999</i>	Date <i>May 10, 1999</i>
Signature of Inventor 4 <i>Chin-Yuan CHEN</i> Chin-Yuan CHEN	Signature of Inventor 5 <i>Chienchia CHIU</i> Chienchia CHIU	Signature of Inventor 6 <i>Chenn-Shiung CHENG</i> Chenn-Shiung CHENG
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